SYNTHESIS OF NANO/MICROSTRUCTURES BY USING BIOMEMBRANES

SHORT SYNOPSIS

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by

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Certificate

I hereby declare that the short synopsis "**Synthesis of Nano/Microstructures by Using Biomembranes**" being submitted in partial fulfillment of the requirement for the degree of Doctor of Philosophy in Electronics and Communication Engineering under Faculty of Engineering and Technology of Manav Rachna International Institute of Research & Studies, Faridabad during the academic year 2013-14.

It is a bonafide record of original work carried out under the supervision of Dr. Devi Singh, Dr. R. P. Chauhan and Dr. S. K. Chakarvarti. It has not been submitted in full or part to any other university or institute for degree or diploma. Further, it is certified that short synopsis is plagiarism free and proof has been submitted.

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ABSTRACT

From past decades, materials at nano and micro scales have gathered lot of attention from researchers worldwide. These materials have marvelous and different characteristics from their bulk. They have engrossed wide consideration because of distinctive chemical and physical properties, and thus made them suitable candidates for various useful applications.

From the past few years, biological templates have become very popular for the synthesis of various nano and micro structures. Over the conventional assembly methods, use of biological templates to form nanostructures are helpful as they are energy-conserving, green and inexpensive. They have great prospective in research area. Earlier, shell membrane, mushroom gills, silk fiber, spider silk, insect wings, bacterial cellulose membranes, cotton/cloth textile, wool, living cells, paper, pollen grains, skeletal plates, and wood were used as biological templates for the syntheses of inorganic structures (silicon dioxide, titanium dioxide, copper oxide, aluminum oxide, and iron oxide etc.). In the present work, negative template synthesis will be used for fabrication of nanostructures especially chalcogenides like Ag_2S or PbS. The method adopted will be simple capillary action of epidermal layer of biomembranes used.

Key words: Bio membranes, Bio Template synthesis, Negative Templates, capillary action

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1. Introduction

Material at atomic and molecular scale with at least one dimension 1-100 nm is Nanotechnology. Due to interdisciplinary nature, it found applications in all walks of life- like medicine, electronics, biomaterials energy production, and consumer product for betterment of society. It includes variety of techniques for material fabrication and their characterization. Environment is full of sophisticated decidedly well-ordered nanostructures, are not easy to make through cut-edged technologies. So researchers are attentive in search of naturally available bio materials help in creating copies of their own morphologies and thus fabricated materials have enriched features like control in size, crystalline structure and their surface chemistry.

For fabricating nanomaterials, there are two methods in general:

(i) Top-down approach, i.e., breakdown of bulk material in smaller pieces using any form of energy like mechanical, chemical or other form of energy and **(ii) Bottom-up approach,** i.e., material is fabricated via chemical reactions from atomic or molecular species, precursor particles to grow in dimensions. Schematic diagram illustrating top-down and bottom-up approaches is shown in Fig. 1.1

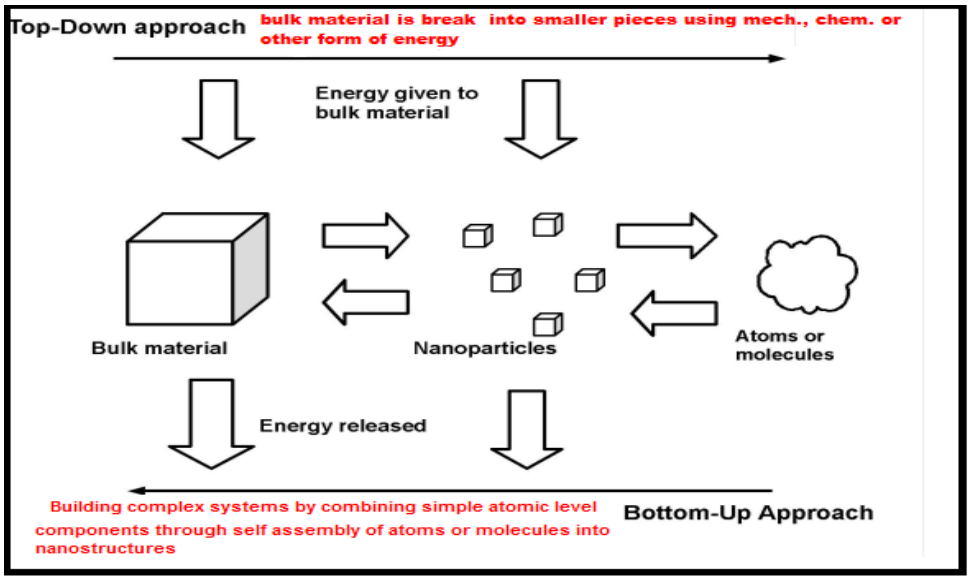
Top-Down approach
bulk material is break into smaller pieces using mech., chem. or other form of energy
Energy given to bulk material
Bulk material
Nanoparticles
Atoms or molecules
Energy released
Building complex systems by combining simple atomic level components through self assembly of atoms or molecules into nanostructures
Bottom-Up Approach

Fig 1.1 Methods for fabricating nanomaterials

Out of these two methods, the bottom-up methodology is a good choice of researchers worldwide as top down approach produces defects on the superficially, result in change in physical characteristics and the superficial chemistry of the nanostructures formed. For example, superficial defects may have decreased conductivity due to inelastic surface scattering; causing excessive heat generation. Such properties proved to be major hindrances in device fabrication. However, bottom-up methodology make nanostructures with less numbers of defects and have more consistent chemical configuration.

2. Literature Review

In recent times, low dimensional assemblies are favorite choice of researchers because of outstanding improved physical and chemical properties than conventional materials. Changed properties leads to prospective applications in diverse fields like catalyst, medical, electronic field, ceramics, colorants, sensors, powder and paint. Similar work is done by (Black et al. 2002). He worked on Bismuth nanowires having decreased particle size, resulting in optical non linearity to provide better optics characteristics.

As discussed before these low dimensional assemblies can be fabricated by top down and bottom up approach. Techniques used under these two approaches are highly edge-cutting. Besides being expensive choice they may have uncontrolled dimensions, crystalline structure. Therefore there is a need of developing simplistic and green technologies leads to nanomaterials fabrication. From past time, news of production of inorganic constituents via bio structures are common. Here, some common techniques under top down and bottom up methodologies and growth in bio template synthesis is mentioned.

2.1 Top-Down Approach

Techniques like slow destruction by mechanical energy, methods using concept of Lithography and Scanning Tunneling Microscopy are common examples of top-down methodology this approach is based on two factors, by “sculpting” method for making nanostructures. It embraces etching (dry / wet), mechanical attrition, lithographic methods. They help in making materials of required shape. Mechanical Attrition form composites, ceramics nano dimensions. Lithographic based techniques are economical and fast. (Ito and Okazaki 2000) had fabricating

nano dimensioned assemblies with dimension less than 69 nm by photo lithographic technique. (Penmatsa et al. 2012) had fabricated nanostructures by photolithography (Kurihara et al. 1995) built Si nanowires and pillars of 10-nm by electron beam lithography.

In case of another parameter nanostructures are created by addition or organizing required material on substrate. There are numerous techniques which are based on mentioned principle, such as colloidal dispersion. (Visca 1979) had prepared nanoparticles of TiO_2 by colloidal dispersion. Liquid pioneer of required components make aerosol and after its solidification, it forms particles in spherical shapes. Size of such nanoparticles are dependent on liquid drip dimension and solid composition. However, microscopy methods which are non-optical, use tunneling principle for arranging atoms in desired patterns. Such methods may result in Nano dots, nano lines of dimension of sun nanometers. For example, on Silicon, corrals of Gold was produced by (Hu et al. 1999).

2.2 Bottom-Up Approach

Here assemblies at atomic level progress to create required structures. There is a progression of individual atoms/molecules to combine and form nanostructures. It includes template synthesis of nanostructures by nucleation process resulting in nanostructures of precise shape and size. Techniques like Evaporation and Condensations, Sputtering, Chemical and Physical Vapor Desposition, Epitaxy use Bottom-Up Approach. Researchers like (Sean 1955) developed Hg nanowires of 200 nm diameter.

The bottom-up approach is widely chosen over top-down approach, because it lead to defects superficially to have substantial effect on the physical characteristics and the superficial interaction of nanostructures created. Fabrication of nanostructures using templates is an emerging method considered as equivalent method when compared with bottom up synthesis.

2.3 Templates

Conventional techniques are hi-tech as discussed but have of their own shortcomings and difficulties. Requirement of substitute technique in terms of robustness, efficiency and handling is needed. Template synthesis is an alternative approach which is simple to use. It is

a membrane based technique (Chakarvarti 2006). It is a configuration/ mold which help in fabricating assemblies identical as their own morphological construction. Researchers all over the world are using this simple and innovative technique for fabricating nanomaterials of various classes that include metals, nonmetals, semiconductors, polymers, wires of variable proportions and sizes. Template synthesis can be of three types (depending on mode of synthesis). Negative Template Method, Positive Template Method and Surface Step Edge Template Method. Out of which, **Negative Template Synthesis** is favorite technique of researches worldwide. It is a process of filling and depositing inside template pores with desired material. It can be done by process like electrochemical technique. After that template is itched and we get free standing structures which are exact replica of their respective templates in respect of topology and morphology. (Possin 1970) used Mica template for fabrication of nanostructures of around 400 A^0. He used electro deposition technique for filling the pores. (Riveros 2006) fabricate Silver nanowires through pore filling After that metallic (Wang et al. 2001); Yoo et al. 2006); (Kaniyankandy et al. 2007); (Ohgai et al. 2003), semiconducting (Liu et al. 2006), compound semiconducting (Jin-Xu et al. 2006); Joshi and (Lokhande 2007), alloys (Kazeminez and Schwarszacher 2006); (Abid et al. 2006), (Xu et al. 2006), metal-semiconductor heterostructures (Chakarvarti and Vetter, 1993 & 1996) and multilayered (Valizadeh et al. 2002); (Nielsch et al. 2005) nanomaterials and nanostructures were formed. In **Positive Template Method**, required material is set down outside of template surface and result in formation of wire shape nanostructures. For example, DNA can be used to build artificial nanostructures as done by (Sun et al. 2005).In **Surface Step Edge Templates,** selected material is deposited on defect sites of the substrate.

Bio templates are natural and organic by nature. They are advantageous due to their well-ordered geometry. Nanomaterials fabricated by biomembranes have enhanced physical characteristics. Nature has variety of bio templates, belong to different classes of plants and animals origin. They help in fabricating diverse nano structures but few are of technical interest and briefly discussed. Butterfly wings results nanostructures with better optical characteristics used to produce photonic sensors. They are rich in atomic scales with multiple layers and air in between, results in multiple reflection of light in whole visible range spectrum and reduces at ultraviolet range. (Wang et al. 2014) created optical electronic devices through butterfly

wings. Here 200-400 nm ZnO nanoparticles are filled in wings to act as emitting gain media. Zhang et al (2008) developed dye-sensitized solar cell by using butterfly wing scales. Here Titania photo anodes were used. In 2006, he created ZnO nano tubules. (Huang et al. 2006) have developed Al_2O_3 coating through butterfly wings for photonic devices.

Another class of unicellular microorganisms like Diatoms have silica cell walls with well-defined unique geometrical patterns based on species used. These geometric patterns help in making exact copy of nanostructures. Various examples reported include metal coated nanoparticles by (Payne et al. 2005) for Raman spectroscopy. (Zhou et al. 2007) had used various species in Bacteria for synthesizing ZnS nanostructures. Similarly (Mogul et al. 2005) worked on E.coli and Rhodospriliumrubrum for synthesizing Ni nanoparticles. Virus, for example Tobacco Mosaic Virus are successfully used for creating nanostructures worldwide (Love et al. 2005) had produce Gold nanoparticles. Here, these researches emphasis on the design, synthesis, characterization and application of nanostructures. The examples of these nanostructures include quantum dots, quantum wires, nanotubes, nanorods by (Nouroozi et al. 2011), nanofibres by (Selvakumar et al. 2014), nanofoams by (He et al. 2014), nanocrystals by (Shang et al. 2010), ZnO hexagonal prisms by (Preda et al. 2018), $MgCr_2O_4$ nanomaterial using egg shell membrane by (Tholkappiyan and Fathalla 2016). These above mentioned nanostructures were formed with the help of biotemplates. The advantage of bio membranes over usual templates is, they are inexpensive and they remain stable.

2.4 Gap in Literature

Though there are various methods like milling to lithography techniques for fabrication of nanostructures but they have disadvantages like uncontrolled morphology design and geometry and aspect ratio. However template synthesis technique rectifies the above mentioned troubles, whether it is aspect ratio or desired geometry. Nanostructures so formed are exact duplication of template pores in respect of morphology, geometry or stereo-chemical features. The deposition process takes place by many techniques like electrodeposition, electroless deposition, pressure injection techniques, chemical vapor deposition etc. Here, filling of the

templates with the preferred material can be done by simple capillary action of cellular structure of biomembranes used.

3. Description of Broad Area

Biomembranes for example inner layer of Allium Cepa or Egg Shell membrane are porous in nature. In general, onion cell shape is rectangular or square and closely packed. Cell membrane is made of three layers: sugar-chain layer, lipid layer and protein layer. It is rich in functional groups which are important in formation of nanomaterials. When a dry epidermal layer is kept in between two solutions at different concentrations. The molecules of one solutions are attracted to the molecules of onion cells, they come in contact with molecules of another solution lying on the other side of membrane, resulting in the chemical reaction and thus formation of nanostructures. For example if solutions of $AgNO_3$ and Na_2S are taken at concentration of 0.2 M and 0.1 M respectively and epidermal layer of Allium Cepa is sandwiched between two solutions, then Ag^+ ions may pass cell membrane and react with hydroxyl groups present on cell membrane. When S^{2-} ions from Na_2S from other side meet Ag^+ ions and form Ag_2S crystal nuclei at the surface.

4. Objective of the Study

4.1 Problem formulation

So far we have discussed sophisticated methods for fabricating various nanostructures. These techniques include milling to lithography techniques which have huge and expensive set up. Nanostructures also suffer disadvantages like uncontrolled morphology design and geometry and aspect ratio. Thus, a technique is needed to avoid such complications which should be simple, easy and robust. Hence technique discussed here is green, simple to use and robust in nature.

4.2 Objectives

The objective of this work is to synthesis nanostructures using biomembranes which are simple and easy in use.

(i) To study various kind of bio membranes like squama layer of onion, garlic bulb egg shell membrane and their respective pore shapes and size.

(ii) To study capillary action in bio membranes.

(iii) To study difference in various techniques and capillary action for developing nanoparticles via biomembranes.

(iv) To develop nanoparticles with the help of selected bio membranes by using capillary action.

(v) To study characterization techniques used for characterize nanoparticles.

(vi) To study changes in physical properties of nanoparticles formed with respect to bulk materials.

5 Methodology to be adopted

For fabricating nano/microstructures following steps will be into consideration:

i. **Searching of Bio membranes and compatible materials:** Bio membranes which are easily available and abundant in nature. They should be easy to handle. For example Squama inner layer of Allium Cepa, Egg Shell Membrane. Depending on the type of membrane, compatible materials will be found which can easily nucleate on selected bio membrane, for example Silver Nitrate (Ag_2NO_3).
ii. **Apparatus Development:** An apparatus will be developed to mount the biomembranes. This apparatus will be helpful for various reactions to take place to form nanostructures.
iii. **Characterization of Nano/Microstructures:** Formed nanostructures can be confirmed by characterization techniques like Transmission Electron Microscopy, Scanning Electron Microscopy, X-ray Diffraction Technique (XRD), Fourier Transform Infra-Red Technique (FTIR), UV-Visible spectroscopy.

6. Expected outcome of the research

Proposed work will help in fabricating nanostructures through biomembranes that exist easily in nature. Hence to accomplish this research it is important to choose biomembranes from wide variety of availability which are appropriate in handling and selecting of bio- membrane compatible materials to fabricate nano / micro structures. Developing of nanoparticles with the help of capillary action. Structures formed are then characterized by various techniques

like Scanning Electron Microscopt, FTIR, UV-Visible Spectroscopy to study their physical properties and how they are different from respective bulk materials. Study of properties will help in developing real time applications like biosensors.

7. Proposed Time Frame (Gantt Chart)

Research Plan														
	Sem 1 (June '14)	Sem 2 (Dec' 14)	Sem 3 (June '15)	Sem 4 (Dec' 15)	Sem 5 (June '16)	Sem 6 (Dec' 16)	Sem 7 (June '17)	Sem 8 (Dec' 17)	Sem 9 (June '18)	Sem 10 (Dec' 18)	Sem 11 (June '19)	Sem 12 (Dec' 19)	Sem 13 (June '20)	Sem 14 (Dec' 20)
Course Work														
Literature Review														
International Paper Presentation And Publication														
Data Collection														
Data Study														
Interpretation of Data														
Thesis Submission														

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